APPENDIX B

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THE INFLUENCE OF pH ON THE PERFORMANCE OF ORGANOSILICONE SURFACTANTS

REFERENCE: Policello, G.A., Stevens, P.J.G., Forster, W.A. and Murphy, G.J., **"The Influence of pH on the Performance of Organosilicone Surfactants,"** Pesticide Formulations and Application Systems: 14th Volume, ASTM STP 1234, Franklin R. Hall, Paul D. Berger, and Herbert M. Collins, Eds., American Society for Testing and Materials, Philadelphia, 1995.

ABSTRACT: Trisiloxane based spreading agents are a unique class of surfactants that enhance spray coverage and, in many cases, increase the uptake of agrochemicals into plant tissue through stomatal flooding. The degree of uptake is closely related to the spreading ability of these surfactants. Solution pH is a key influence on the performance of trisiloxanes. These materials undergo rapid hydrolysis at extremes in pH, and therefore show a marked decrease in spreading and uptake of chemicals into leaf tissue. Buffering solutions of the trisiloxane surfactants to a neutral pH increases their hydrolytic stability from hours to > 2 years.

KEYWORDS: organosilicone surfactant, SILWET L-77®, surfactant, L-77, trisiloxane, hydrolysis, trisiloxane ethoxylate, stomatal uptake, spreading, spray coverage.

THE INFLUENCE OF pH ON SPREADING

Organosilicone surfactants have been shown to enhance the spreading and coverage of pesticidal spray solutions on difficult-to-wet plant surfaces relative to conventional surfactants (Zabkiewicz et al. 1988). Some of the key factors influencing spreading are related to the low aqueous surface tension ($\leq$21 mN/m at 0.1 wt%) and the compact structure of the trisiloxane (Ananthapadmanabhan et al. 1990). In addition, the stability and subsequent performance of these unique surfactants is strongly influenced by pH (Knoche et al. 1991; Murphy et al. 1991).

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Spreading was determined by applying 10 µL of a surfactant solution onto a polyester film (IR 1175 or AF 4300; 3M) and measuring the spread diameter after 30 seconds. Stock surfactant solutions were prepared in pH Buffer solution (pH 3, 5, 7 and 10). Spreading was measured as a function of solution age.

Table 1 demonstrates that 0.1 wt% solutions of SILWET L-77® (trisiloxane ethoxylate; TSE)[1,3] buffered at pH 3, pH 5 and pH 10 show a reduction in spreading ability with solution age. The trisiloxane undergoes rapid hydrolysis at pH 3 and pH 10 showing a significant loss in spreading within the first hour. Although at pH 5 hydrolysis proceeds at a slower rate, a loss of spreading is observed for solutions with an age of greater than 8 days.

TABLE 1--Influence of pH on spreading

	Spread diameter, mm[a]			
Time	pH 3	pH 5	pH 7	pH 10
15 min	38	49	46	--
30	--	--	--	19
60	10	--	--	--
1 day	4	39	49	8
8	4	6	42	4
17	4	5	44	4
30	--	--	44	--
196	--	--	31	--

[a] Spreading of 0.1 wt% TSE on polyester film (water = 4 mm)

Buffering the solution to pH 7 significantly increases the trisiloxane's resistance to hydrolysis (Table 1). Even at neutral pH, this low concentration solution (0.1 wt%) of the trisiloxane (pH 7) will eventually show a reduction in spreading. For example this same solution of the trisiloxane with an age of > 196 days (6.5 months) has retained approximately 67% of its initial spreading (Spread Diameter = 31 mm vs 46 mm).

Using a concentrated dispersion buffered to pH 7 increases the resistance to hydrolysis significantly. A 10 wt% dispersion of TSE containing buffer maintained over 95% of its spreading ability for > 2 years, whereas a similar dispersion without buffer showed a significant loss in spreading after 8 months (< 10% of the initial spreading).

[3] α-1,1,1,3,5,5,5-heptamethyltrisiloxanylpropyl-ω-methoxy-poly(ethylene oxide) mean 8EO

EFFECT OF pH ON PLANT UPTAKE

Trisiloxane surfactants have been shown to increase the uptake of chemicals into plant tissue through stomatal infiltration (Stevens et al. 1991). The same factors that influence spreading apply to the trisiloxane's ability to promote chemical uptake.

Stomatal infiltration (uptake within 10 minutes of application) of ^{14}C deoxyglucose (DOG) into bean leaf (*Vicia faba*) was determined using methods previously reported by Stevens et al. (1991). Applications were made during the plants photoperiod, excluding the first and last hours to ensure that the stomata were open. The treatment solutions were made up at pH 3, pH 5, pH 7 and pH 10, in universal buffer (Dawson et al. 1969). Phenyl mercuric acetate was used at 10 mg/L to inhibit microbial growth. Solutions were aged in the same controlled environment used for plant growth and treatment throughout the study (20°C/15°C; day/night).

The effect of pH on DOG uptake was determined by applying solutions of increasing age of DOG containing TSE and buffer to bean leaf, and measuring the uptake after 10 minutes.

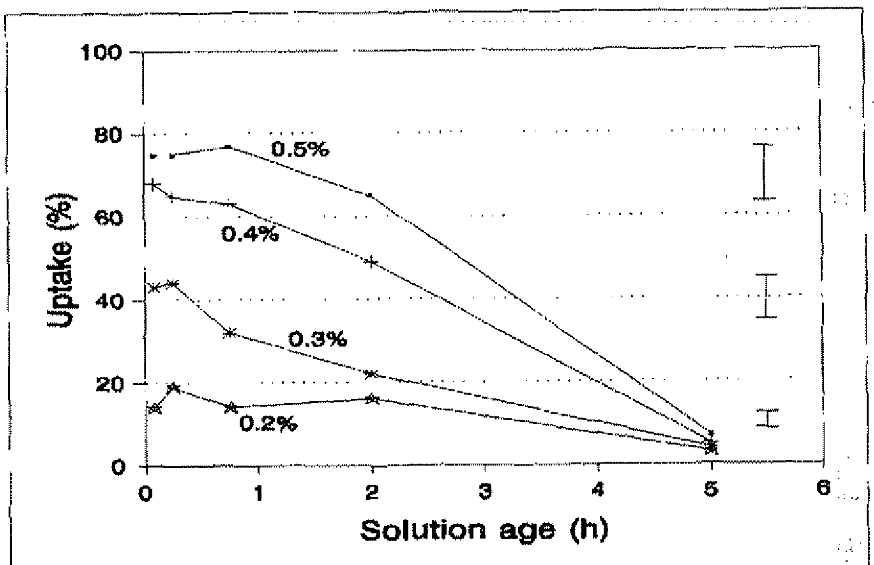

FIG. 1--Effect of TSE concentration and age of solution (pH 3) on stomatal infiltration.

The effect of pH on performance is illustrated in Figure 1, where the uptake of ^{14}C tagged DOG into bean was monitored for solutions containing the trisiloxane. The initial treatment shows an increase in uptake, with an increase in the TSE concentration, such that uptake from freshly prepared solutions increased from 45% at 0.3% TSE to 75% at 0.5% TSE. However, the overall uptake of DOG decreases with increasing sample age, as the trisiloxane hydrolyzes at pH 3.

Likewise, Figure 2 demonstrates that the ability of the trisiloxane (0.5 %) to promote uptake of DOG is significantly diminished with an increase in solution age at pH 5 and 10. Although the rate of hydrolysis is not as dramatic as at pH 3, the result is the same. The uptake of DOG continues to decrease with increasing solution age. As with spreading, this indicates a rapid hydrolysis of the trisiloxane. Eventually the effects of the hydrolysis are so severe that uptake declines to a level similar to that observed for DOG solutions without trisiloxane (Stevens et al. 1991).

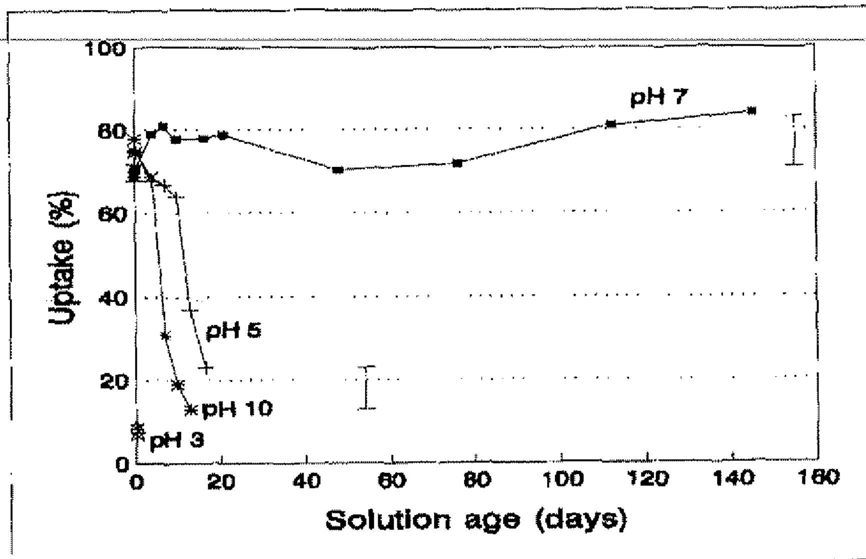

FIG. 2--Effect of pH and age of solution on stomatal infiltration.

Figure 2 also illustrates that treatment solutions buffered at pH 7 retain the ability to promote DOG uptake for an extended shelf-life period.

Both spreading and uptake of DOG are significantly influenced by the pH environment of the treatment solution. This also suggests that the spreading ability of the trisiloxane and the uptake of the DOG are closely related (Compare with Table 1).

This slow hydrolysis of trisiloxane ethoxylate solutions and dispersions, especially at higher concentration, and under neutral pH, offers an effective method for incorporating these products in pesticidal formulations, with improved shelf life.

SUMMARY

The spreading efficiency of trisiloxane surfactants is reduced under acidic (pH 3, pH 5) or alkaline conditions (pH 10), while spreading is maintained at pH 7.

Stomatal infiltration increases with an increase in the trisiloxane concentration, as measured by ^{14}C DOG uptake into bean at 10 minutes after application.

Uptake of DOG declined with increasing solution age at pH 3, pH 5 and pH 10, while treatment solutions buffered at pH 7 retained uptake efficacy.

The aqueous stability, and subsequent spreading and uptake are significantly influenced by the pH environment of the treatment solution, and appear to be related.

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